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(54) Title: FILLED CUT-RESISTANT FIBER

(57) Abstract

A fiber having increased cut resistance is made from a fiber-forming polymer and a hard filler having a Mohs Hardness Value greater than about 3. The filler is included in an amount of about 0.05 % to about 20 % by weight. In preferred embodiments, the fiber-forming polymer is poly(ethylene terephthalate) or a liquid crystalline polyester comprising monomer units derived from 6-hydroxy-2-naphthoic acid and 4-hydroxybenzoic acid. Preferred fillers include tungsten and alumina.

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FILLED CUT-RESISTANT FIBER

Field of the Invention

This invention relates to a filled fiber having improved resistance to cutting.

Background of the Invention

Small amounts of particulate titanium dioxide can be used in polyester fiber as a delustrant. Also used in polyester fiber is a small amount of colloidal silicon dioxide, which is used to improve gloss. Magnetic materials have been incorporated into fibers to yield magnetic fibers. Examples include: cobalt/rare earth element intermetallics in thermoplastic fibers, as in published Japanese Patent Application No. 55/098909 (1980); cobalt/rare earth element intermetallics or strontium ferrite in core-sheath fibers, described in published Japanese Patent Application No. 3-130413 (1991); and magnetic materials in thermoplastic polymers, described in Polish Patent No. 251,452 and also in K. Turek et al., J. Magn. Magn. Mater. (1990), 83 (1-3), pp. 279-280.

Various kinds of gloves have been made in which metal has been included in the fabrication of the glove to impart protective qualities to the glove. For example, U.S. Patent Nos. 2,328,105 and 3,185,751 teach that a flexible, X-ray shield glove may be made by treating sheets of a suitable porous material with a finely divided, heavy metal which may be lead, barium, bismuth or tungsten, or may be made from a latex or dispersion containing heavy metal particles. As illustrated by U.S. Patent No. 5,020,161, gloves providing protection against corrosive liquids have been made with a metal film layer.

Cut-resistant gloves are beneficially utilized in the meat-packing industry and in automotive applications. As indicated by U.S. Patent Nos. 4,004,295, 4,384,449 and 4,470,251, and by EP 458,343, gloves providing cut resistance have been made from yarn which includes flexible metal wire or which consists of high tensile strength fibers.

A drawback with gloves made from yarn that includes flexible metal wire is hand fatigue with resultant deceased productivity and increased likelihood of injury. Moreover, with extended wear and flexing, the wire may fatigue and break, causing cuts and abrasions to the hands. In addition, the wire will act as a heat sink when a laundered glove is dried at elevated temperatures, which may reduce tensile strength of other yarn fiber, thereby decreasing glove protection and glove life.

Improved flexibility and uncomplicated laundering are desirable in cut-resistant, protective apparel. Therefore, there is a need for a flexible, high tensile strength, cut-resistant fiber that retains its properties when routinely laundered and that resists flexural fatigue. Such a fiber may be advantageously used in making protective apparel, in particular highly flexible, cut-resistant gloves.

Summary of the Invention

A cut-resistant fiber is made from a fiber-forming polymer by including a hard filler distributed uniformly in the fiber. The hard filler has a Mohs Hardness value greater than about 3 and is present in an amount of about 0.05% to about 20% by weight. The fiber has improved cut resistance properties compared with the same fiber without the hard filler. A method of making cut-resistant fabric is also taught. In this method, a uniform blend of a fiber-forming polymer and

about 0.05% to about 20% by weight of a hard filler having a Mohs Hardness value greater than about 3 is made. The uniform blend is spun into a fiber or yarn, which is then fabricated into fabric having improved cut resistance in comparison with fabric made from the same fiber-forming polymer without the hard filler. The cut-resistant fabric may optionally also include other polymeric fibers and/or reinforcing inorganic fibers, which may be ceramic, metal or glass.

Detailed Description of the Invention

As indicated above, a flexible cut-resistant fiber useful for the manufacture of protective apparel may be produced when a hard filler is included in the fiber. The fiber may be made of any fiber-forming polymer, and may be produced by any of the methods normally used in making fibers. The polymer preferably is melt processable, in which case, the cut-resistant fiber is typically made by melt spinning. For polymers that cannot be spun into fibers in the melt, wet spinning and dry spinning may also be used to produce fibers having improved cut resistance. Amorphous polymers, semi-crystalline polymers and liquid crystalline polymers may all be used in this invention. Of these, semi-crystalline and liquid crystalline polymers are preferred.

In one preferred embodiment of this invention, the fiber-forming polymer is an isotropic semi-crystalline polymer. Preferably, the semi-crystalline polymer is melt processable; i.e., it melts in a temperature range which makes it possible to spin the polymer into fibers in the melt phase without significant decomposition. Semi-crystalline polymers that will be highly useful include poly(alkylene terephthalates), poly(alkylene naphthalates), poly(arylene sulfides), aliphatic and aliphatic-aromatic polyamides, and polyesters comprising monomer units derived from cyclohexanedimethanol and terephthalic

acid. Examples of specific semi-crystalline polymers include poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate), poly(phenylene sulfide), poly(1,4-cyclohexanedimethanol terephthalate), wherein the 1,4-cyclohexanedimethanol is a mixture of cis and trans isomers, nylon-6 and nylon-66. The preferred semi-crystalline isotropic polymer is poly(ethylene terephthalate). Isotropic polymers that cannot be processed in the melt can also be used, as for example rayon, which is typically dry spun using acetone as a solvent, and poly [2,2'-(m-phenylene)-5,5'-bibenzimidazole], generally referred to as polybenzimidazole, which is typically wet spun using N,N'-dimethylacetamide as a solvent. Amorphous, non-crystalline, isotropic polymers, such as the copolymer of isophthalic acid, terephthalic acid and bisphenol A (polyarylate) may also be filled and utilized in this invention.

In another preferred embodiment, the fiber is made from a liquid crystalline polymer (LCP). LCPs give fibers with very high tensile strength and/or modulus. The liquid crystalline polymer may be processable in the melt (i.e., thermotropic), in which case melt spinning is the preferred method of making the fiber. However, polymers that cannot be processed in the melt may also be utilized. Thus, polymers that exhibit liquid crystalline behavior in solution can be blended with a hard filler and then can be wet or dry spun to yield cut-resistant fibers in accordance with the present invention. For example, the aromatic polyamide made from p-phenylenediamine and terephthalic acid (as for example polymers sold under the KEVLAR® trademark) can be filled and wet spun to yield a cut-resistant fiber, provided that the hard filler does not react with or dissolve in the solvent.

The preferred liquid crystalline polymers (LCPs) for use in this invention are thermotropic LCPs. These thermotropic LCPs include aromatic polyesters, aliphatic-aromatic polyesters, aromatic poly(esteramides), aliphatic-aromatic poly(esteramides), aromatic poly(esterimides), aromatic poly(estercarbonates), aromatic polyamides, aliphatic-aromatic polyamides and poly(azomethines). The preferred thermotropic LCPs are aromatic polyesters and poly(esteramides) which form liquid crystalline melt phases at temperatures less than about 360°C and include one or more monomer units derived from terephthalic acid, isophthalic acid, 1,4-hydroquinone, resorcinol, 4,4'-dihydroxybiphenyl, 4,4'-biphenyldicarboxylic acid, 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 2,6-naphthalenedicarboxylic acid, 2,6-dihydroxynaphthalene, 4-aminophenol, and 4-aminobenzoic acid. Some of the aromatic groups may include substituents which do not react under the conditions of the polymerization, such as lower alkyl groups having 1-4 carbons, aromatic groups, F, Cl, Br and I. The synthesis and structure of some typical aromatic polyester are taught in U.S. Patent Nos. 4,473,682; 4,522,974; 4,375,530; 4,318,841; 4,256,624; 4,161,470; 4,219,461; 4,083,829; 4,184,996; 4,279,803; 4,337,190; 4,355,134; 4,429,105; 4,393,191; and 4,421,908. The synthesis and structures of some typical aromatic poly(esteramides) are taught in U.S. patent Nos. 4,339,375; 4,355,132; 4,351,917; 4,330,457; 4,351,918; and 5,204,443. Aromatic liquid crystalline polyesters and poly(esteramides) are available from Hoechst Celanese Corporation under the VECTRA® trademark, as well as from other manufacturers.

The most preferred liquid crystalline polyester comprises monomer repeat units derived from 4-hydroxybenzoic acid and 6-

hydroxy-2-naphthoic acid, as taught in U.S. Patent No. 4,161,470. Preferably, monomer units derived from 4-hydroxybenzoic acid comprise about 15% to about 85% of the polymer on a mole basis, and monomer units derived from 6-hydroxy-2-naphthoic acid comprise about 85% to about 15% of the polymer on a mole basis. Most preferably, the polymer comprises about 73% monomer units derived from 4-hydroxybenzoic acid and about 27% monomer units derived from 6-hydroxy-2-naphthoic acid, on a mole basis. This polymer is available in fiber form under the VECTRAN® trademark from Hoechst Celanese Corporation, Charlotte, North Carolina.

Other preferred liquid crystalline polyesters or poly(esteramides) comprise the above recited monomer units derived from 6-hydroxy-2-naphthoic acid and 4-hydroxybenzoic acid, as well as monomer units derived from one or more of the following monomers: 4,4'-dihydroxybiphenyl, terephthalic acid and 4-aminophenol. A preferred polyester comprising these monomer units is derived from 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-biphenol and terephthalic acid, as taught in U.S. patent No. 4,473,682, with the polymer comprising these monomer units in a mole ratio of about 60:4:18:18 being particularly preferred.

A preferred poly(esteramide) comprises monomer units derived from 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, terephthalic acid, 4,4'-biphenol and 4-aminophenol, as taught in U.S. Patent No. 5,204,443; a highly preferred composition comprises these monomer units in a mole ratio of about 60:3.5:18.25:13.25:5.

An important aspect of this invention is the discovery that a flexible, flexural fatigue-resistant and cut-resistant fiber may be made from a suitable polymer filled with a hard material that imparts cut resistance. The material may be a metal, such as an elemental metal

or metal alloy, or may be nonmetallic. Generally, any filler may be used that has a Mohs Hardness value of about 3 or more. Particularly suitable fillers have a Mohs Hardness value greater than about 4 and preferably greater than about 5. Iron, steel, tungsten and nickel are illustrative of metals and metal alloys, with tungsten, which has a Mohs value ranging from about 6.5 to 7.5 being preferred. Non-metallic materials are also useful. These include, but are not limited to, metal oxides, such as aluminum oxide, metal carbides, such as tungsten carbide, metal nitrides, metal sulfides, metal silicates, metal silicides, metal sulfates, metal phosphates, and metal borides. Other ceramic materials may also be used. Titanium dioxide and silicon dioxide are less preferred in semi-crystalline polymers.

A particulate form of the filler may be used, with a powder form being generally suitable. Selection of an appropriate particle size depends on the processing and on the fiber diameter. The filler particles should be small enough to easily pass through the spinneret apertures. The particles should also be small enough that the fiber tensile properties do not appreciably deteriorate. In general, the particles should have an average diameter of less than about 20 microns, preferably in the range of about 0.05 to about 5 microns, and most preferably in the range of about 0.2 to about 2 microns. For elongated particles, the long dimension should fit through the spinneret holes. Therefore, the average particle length of an elongated particle should be less than about 20 microns, desirably is in the range of about 0.05 to about 5 microns, and preferably is in the range of about 0.2 to about 2 microns.

A minor percentage of the hard filler is used. The amount is chosen to yield enhanced cut resistance without causing a significant loss of tensile properties. The cut resistance of the fiber or fabric

made from the fiber is improved, preferably by at least about 10%, using tests generally accepted in the industry. Such tests as applied to fibers of liquid crystalline polymers are described in Example 3, and as applied to fibers of isotropic polymers are described in Example 4. The tensile properties of the fiber (tenacity and modulus) should not decrease more than about 50% and preferably will not decrease by more than about 25%. Most preferably, there will not be a significant change in tensile properties (i.e., less than about 10% decrease in properties). On a weight basis, the filler is present in an amount of about 0.05% to about 20%. On a volume basis, the amount of filler is typically in the range of about 0.01% to about 3%, preferably in the range of about 0.03% to about 1.5%, and more preferably in the range of about 0.05% to about 1%, with the proviso that the amount of filler is not greater than about 20% on a weight basis. Thus, for a dense filler, such as tungsten powder in poly(ethylene terephthalate), the amount of filler corresponding to the volume percents stated above but expressed on a weight basis, is typically in the range of about 0.14% to about 20%, preferably in the range of about 0.42% to about 20%, and more preferably in the range of about 0.7% to about 14%. For PET, excellent properties are obtained with about 0.7% by volume of filler, corresponding to about 10% by weight when tungsten is the filler. For thermotropic liquid crystalline polymers, excellent cut resistance is obtained with about 0.07% to about 0.14% by volume of filler, corresponding to about 1% to about 2% by weight when the filler is tungsten.

In accordance with the present invention, filled fibers are prepared from a filled resin. The filled resin is made by any of the standard methods for adding a filler to a resin. For example, for a thermoplastic polymer, the filled resin is conveniently prepared in an

extruder by mixing the hard filler with molten polymer under conditions sufficient to provide a uniform distribution of the filler in the resin. The filler may also be present during the manufacture of the polymer or may be added as the polymer is fed into the extruder of fiber spinning equipment, in which case the blending and spinning steps are nearly simultaneous. Any size fiber may be made according to the present invention. In the manufacture of fabrics and yarns, the fiber will generally have a denier in the range of about 1 to about 50 dpf, preferably in the range of about 2 to about 20 dpf, and most preferably about 3 to about 15 dpf. Cut-resistant monofilaments may also be made by including a hard filler. Monofilaments generally have a diameter of about 0.05 to about 2mm. The fibers are made by conventional fiber spinning processes. The preferred process is melt-spinning, but wet-spinning and dry-spinning may also be used.

Cut-resistant fabric may be knit or otherwise made using a filled fiber in accordance with the present invention by using conventional methods and machinery. Such fabric will have improved cut resistance in comparison with the same fabric made using fiber manufactured from the same polymer without a filler. Ideally, the cut resistance will be improved by at least about 10% when measured using tests generally accepted in the industry for measuring cut resistance.

Cut-resistant apparel may then be made from the cut-resistant fabric described above. For example, a cut-resistant safety glove designed for use in the food processing industries may be manufactured from the fabric. Such a glove is highly flexible and readily cleanable. The filled fiber resists flexural fatigue. Protective medical gloves may also be made using the cut-resistant fibers of this invention. Other uses of the fabrics and monofilaments include side curtains and tarpaulins for trucks, softsided luggage, commercial

upholstery, inflatables, fuel cells, collapsible packaging, airline cargo curtains, firehose sheaths, cut-resistant aprons for use in metal packing, and chaps.

Cut-resistant fiber materials described herein can also be substituted for unfilled polymeric fibers in cut-resistant fabrics, gloves and the like made by conventional methods to give even greater cut resistance. Thus, a cut-resistant fabric utilizing the filled fiber taught herein that is further reinforced by including a reinforcing inorganic fiber such as metal, glass or ceramic fiber, in accordance with current technology should have even greater cut resistance than the same fabric using a conventional fiber. Such fabrics may be made from composite yarns made up of strands of the filled fiber disclosed herein intermingled with strands of the metal, glass or ceramic reinforcing fiber. Alternatively, the reinforcing fiber may be present as a core surrounded by the cut-resistant fibers disclosed herein. Composite cut-resistant yarns of conventional fibers and reinforcing fibers are well known to practioners in the art and can readily be adapted to utilize the filled fibers taught herein as a substitute for conventional fibers.

<u>Example 1. PREPARATION OF FILLED LCP</u>

A tungsten powder-filled, melt-processable LCP is prepared as now described. An LCP (pellet form) (95 wt.%) manufactured under the registered trademark VECTRA® A910 (from Hoechst Celanese Corporation) and tungsten powder (average particle size, 0.5 micron, 5 wt.%) are dried at a temperature above 100°C and then mixed. The resulting mixture is added to the hopper of a vibrating feeder of a Werner and Pfleiderer 28mm ZSK extruder (twin screw), passed onto a vibrating trough, and fed into the extruder. The feeder, trough and throat of the extruder are under a positive nitrogen flow. Molten

polymer at a temperature of 305-310°C containing particulate tungsten exits from the extruder in two strands and is passed through a water bath. Thereafter, the cooled strands are fed into a pelletizer, and the pellets are passed through a #4 sieve to remove pellets with "tails." To ensure a uniform distribution of the particulate filler, the filled pellets are fed into the extruder and the process is repeated.

Example 2. PREPARATION AND EVALUATION OF FILLED LCP FIBER

Filled fiber is melt spun from VECTRA polymer compounded with 1 wt.% of tungsten metal powder, as now described. Chips are fed to the hopper of a conventional extruder, and molten polymer at a temperature of about 320°C containing particulate tungsten issues from the extruder. The mixture is passed to a metering pump (pump speed, 38 rpm; 0.584cc/revolution), then through a conventional filter pack that includes a spinneret screen (15-25 microns), and through a spinneret (hole count, 40; hole diameter, 0.005"; hole length, 0.007"). The resultant filaments converge into a lubricant guide and onto a take up roll (2000 ft./min.), which forwards the filaments to a winder unit. Tungsten powder-filled LCP yarn of about 400 denier (forty filaments) is obtained. The filler is generally uniformly distributed throughout the fiber.

The melt spinning process is repeated with variation (0.1-2.0 wt.% tungsten; extrusion temperature, 310-325°C; pump speed, 12-38 rpm; take-up speed, 500-2000 ft./min.; spinneret hole diameter, 0.005-0.013") to obtain tungsten powder-filled LCP yarns of a variety of deniers (forty filaments) as shown in Table 1. The metal-filled fiber is evaluated for tensile properties on an Instron tensile tester. The results of the property measurements are presented in Table 1. Evaluation is conducted using the following test protocols: for

tenacity, a ten-inch gauge length of the fiber with 2.5 twists per inch with a ten percent strain rate; and for modulus, ASTM D885.

TABLE 1

%W	Denier	Tenacity (gpd)	Modulus (gpd)
1.0	444	7.9	523
"	333	7.4	521
"	642	7.8	507
"	778	8.7	453
0.1	678	8.9	492
0.1	1020	--	--
0.5	639	8.4	516
2.0	439	7.4	474
"	724	7.7	482
"	770	8.1	455
"	847	7.4	444
"	1020	--	--

Note: "gpd" means grams/denier

TABLE 2

	Cycles to Failure
0.1% W	259
0.5% W	249
1.0% W	251
2.0% W	141
Stainless steel wire	2

In addition, as indicated in Table 2, tungsten powder-filled fiber made from VECTRA polymer is evaluated for folding endurance (ASTM D-2176). A one pound weight is used for tension. Stainless steel wire of 0.003" diameter is also tested. The samples are of comparable weight. Each result set forth in Table 2 represents the average value from ten trials. Superior flex/fold resistance is found for the tungsten-filled fiber compared to the stainless steel wire.

Moreover, yarn from VECTRA polymer filled with tungsten powder (0.5, 1.0, 2.0 wt.% W with dpf respectively of 16.0, 19.5 and 11.0) is tested for tenacity loss from laundering. It is important that protective apparel can be repeatedly laundered without losing strength. The following washing procedure is used: Wash for 10 minutes at 60°C in 0.1% concentrated detergent (sold under the registered trademark ARM & HAMMER®) in distilled water. Rinse for 10 minutes at 40°C with distilled water. Fresh detergent/water is used for the wash, and fresh distilled water is used for the rinse. Samples are washed for 1, 3, 5, 10 and 15 cycles, and air dried after the final cycle. No tenacity loss is observed after fifteen wash cycles.

Also, yarn from VECTRA polymer filled with tungsten powder (0.5, 1.0, 2.0 wt.% W, with denier respectively of 624, 406 and 773) is tested for tenacity loss from bleach exposure (2.62% Chlorox, 5.24% Chlorox). Sufficient yarn is wrapped around a perforated stainless steel tube and immersed in the appropriate solution for the designated time (2, 12 and 24 hours). Thereafter, the yarn is rinsed with tap water and air dried. The dry yarn is wound on a small spool and tested using a ten inch gauge length with 2.5 twists per inch with a ten percent strain rate. In excess of 85% strength retention is observed.

Example 3. EVALUATION OF CUT RESISTANCE OF LCP YARN

Gloves made of composite yarn constituted as shown in Table 3 are prepared. The high tensile strength polyethylene fiber is commercially available from Allied Corporation of New Jersey under the trademark SPECTRA®. The high tensile strength aramid fiber is commercially available from DuPont of Wilmington, Delaware under the trademark KEVLAR®.

A glove is slit up the side and one layer of fabric is removed for testing. The fabric is stretched in a circular sample holder 4 inches in diameter and pre-tensioned by applying a two pound force to the center of the circle. The test is performed in an Instron tensile tester. The circular sample holder is clamped into the tensile tester at a 45° angle with respect to the floor. The sample holder is raised in a direction perpendicular to the floor at a speed of 5" per minute so that the fabric meets a stationary (non-rotating) carbide blade at an angle, thereby simulating a slicing action. The fabric is mounted so that the knit of the fabric is perpendicular to the direction of the simulated slicing action. The force required for cutting through the fabric (in pounds) is measured by the tensile tester. The results are shown in Table 3. Comparative examples are labelled C-1 to C-6.

The benefit of a filled, compared to an unfilled, LCP fiber is clearly shown in Table 3. Cut resistance enhancement is particularly apparent when the 439 and 444 denier filled VECTRAN M fibers (Examples 3-3 and 3-4) are compared with the 400 denier, unfilled VECTRAN M fiber (Example C-4). Similar conclusions can be reached by comparing Examples 3-1 and 3-2 with Example C-1. Thus it is readily apparent that the cut resistance of LCP fibers improves when as little as about 1% to about 2% by weight of hard filler is present in the fiber. This is equivalent to about 0.07% to about 0.14% by

volume for tungsten filler. Also shown is the superiority of a filled LCP fiber to an unfilled, high tensile strength polyethylene fiber. The VECTRAN M fiber is also more heat resistant than the polyethylene fiber. The aramid fiber cannot withstand exposure to bleach, so that the filled VECTRAN M fiber is advantageous compared with aramid when the fiber is exposed to bleach during use or laundering.

TABLE 3

	Core	1st Wrap	2nd Wrap	Slash (lb)
3-1	650 denier HS PE	847 denier V/2%W	847 denier V/2%W	5.2
3-2	650 denier HS PE	778 denier V/1%W	778 denier V/1%W	5.8
C-1	650 denier HS PE	750 denier VECTRAN M	750 denier VECTRAN M	4.8
C-2	650 denier HS PE	1000 denier HS aramid	1000 denier HS aramid	4.4
C-3	650 denier HS PE	650 denier HS PE	650 denier HS PE	2.9
3-3	650 denier HS PE	439 denier V/2%W	439 denier V/2%W	4.2
3-4	650 denier HS PE	444 denier V/1%W	444 denier V/1%W	4.1
C-4	650 denier HS PE	400 denier VECTRAN M	400 denier VECTRAN M	2.6
C-5	650 denier HS PE	400 denier HS aramid	400 denier HS aramid	2.5
C-6	650 denier HS PE	375 denier HS PE	375 denier HS PE	2.9

"HS" means high tensile strength; "PE" means polyethylene; "V"

means VECTRAN M

Example 4.

Poly(ethylene terephthalate) fibers incorporating tungsten powder filler are described below. Tungsten has a Mohs Hardness value of about 6.5 to 7.5. Tire yarn grade poly(ethylene terephthalate) (PET), having an intrinsic viscosity of about 0.95 when measured in o-chlorophenol, is obtained from Hoechst Celanese Corporation, Somerville, New Jersey in the form of pellets. A master batch is made by blending the polymer with 10% tungsten powder on a weight basis in a twin screw extruder. The tungsten has an average particle size of about 1 micron. The polymer pellets and tungsten are both dried before blending. The master batch is blended with additional PET in a twin screw extruder to yield blends having 1% and 4% tungsten on a weight basis. The samples are melt spun by forcing the molten blend first through a filter pack and then through a spinneret. The yarn is subsequently drawn off a heated feed roll at 90°C, then drawn over a heated shoe, and finally subjected to a 2% relaxation at 225°C. The yarn is plied for testing of properties. The data are summarized in Table 4. One of the 10% tungsten-loaded fibers is also analyzed for tungsten to ensure that the filler is not filtered out. The analysis of the fiber shows about 8.9% by weight tungsten in the fiber.

Tensile properties. The tenacity, elongation and modulus are measured using ASTM test method D-3822.

Cut resistance. The fiber is first knitted into fabric for the testing of cut resistance. The areal density of yarn in the fabric is measured in ounces/square yard (OSY in Tables 4 and 5). The cut resistance of the fabric is then measured using the Ashland Cut Performance Protection ("CPP") test. The test was carried out at TRI/Environmental, Inc., 9063 Bee Cave Road, Austin, Texas 78733-

6201. In the test, the fabric sample is placed on the flat surface of a mandrel. A series of tests is carried out in which a razor blade loaded with a variable weight is pulled across the fabric until the fabric is cut all the way through. The distance the razor blade travels across the cloth until the blade cuts completely through the cloth is measured. The point at which the razor blade cuts through the fabric is the point at which electrical contact is made between the mandrel and razor blade. The distance required to make the cut is plotted on a graph as a function of the load on the razor blade. The data are measured and plotted for cut distances varying from about 0.3 inches to about 1.8 inches. The resulting plot is approximately a straight line. An idealized straight line is drawn or calculated through the points on the plot, and the weight required to cut through the cloth after one inch of travel across the cloth is taken from the plot or calculated by regression analysis. The interpolated values of the weight required to make a cut after one inch of blade travel across the cloth are shown in Tables 4 and 5 as "CPP", an abbreviation for Cut Protection Performance. Finally, for purposes of comparing the data for different thicknesses of cloth sample, the CPP value is divided by the thickness of the cloth (OSY) to compensate for variations in cloth thickness. This value is shown as CPP/OSY in Tables 4 and 5. The cut resistance data for tungsten-filled PET fiber are presented in Table 4.

Example 5.

In these experiments, PET fiber samples are filled with alumina powder, which is sold commercially under the trademark MICROPOLISH® II as a polishing abrasive. Two different alumina powders are used having average particle sizes of about 0.05 microns and about 1.0 microns. Both are obtained as deagglomerated powders from Buehler, Ltd., Waukegan Road, Lake Bluff, Illinois 60044. The 0.05 micron alumina is gamma alumina with a cubic crystal structure and a Mohs Hardness Value of 8. The 1.0 micron material is alpha alumina having a hexagonal crystal structure and a Mohs Hardness Value of 9. The two alumina powders are blended with PET using the same method as in Example 4 to yield filled PET samples containing alumina at levels of about 0.21%, 0.86%, 1.9% and 2.1% by weight. Measurements of fiber properties and cut resistance are made using the same methods as in Example 4. The data are presented in Table 5.

The data in Tables 4 and 5 show that there is an improvement in cut resistance of at least about 10-20% at all levels of filler used. Both sets of data incorporate filler in the fiber at levels of about 0.07% to about 0.7% on a volume basis. The fiber properties do not appear to significantly degrade with these amounts and sizes of particles.

It is to be understood that the above described embodiments of the invention are illustrative only and that modification throughout may occur to one skilled in the art. Accordingly, this invention is not to be regarded as limited to the embodiments disclosed herein.

Table 4. Cut Resistance of PET Filled with Tungsten

No.	% Tungsten Wt. Volume	Particle Size (microns)	dpf	T/E/M[1]	CPP[2]	OSY[3]	CPP/OSY
Control 1	-- --	--	3.1	6.8/6.7/124	421	7.1	59
Control 2	-- --	--	5.0	--	384	6.8	56
Control 3	-- --	--	5.0	--	589	13.0	45
4-1	1% 0.07%	1 micron	5.0	6.3/9.0/128	589	9.1	59
4-2	1% 0.07%	1 micron	5.6		589	7.3	77
4-3	4% 0.29%	1 micron	6.0	7.2/11.6/109	643	7.0	92
4-4	4% 0.29%	1 micron	5.9	7.0/12.5/100	620	7.3	85
4-5	10% 0.72%	1 micron	11.6	6.3/10.0/123	697	7.5	93
4-6	10% 0.72%	1 micron	7.4	4.1/22.9/75	759	8.5	90
4-7	10% 0.72%	1 micron	6.0	--	670	7.6	89

[1]Tenacity (gpd), Elongation (%), Modulus (gpd), measured using ASTM test method D-3822.

[2]Cut Protection Performance, measured using the Ashland CPP test.

[3]Ounces per Square Yard.

Table 5. Cut Resistance of PET Filled with Alumina

No.	% Alumina Wt.	Volume	Particle Size (microns)	dpf	T/E/M[1]	CPP[2]	OSY[3]	CPP/OSY
5-1	0.21%	.07%	1 micron	11.4	6.7/10.3/112	547	7.2	76
5-2	0.21%	.07%	1 micron	5.6	7.4/12.4/104	463	7.5	62
5-3	0.86%	0.30%	0.05 micron	5.6	7.4/14.0/110	501	7.3	69
5-4	0.86%	0.30%	0.05 micron	5.7	6.9/12.8/110	497	6.7	73
5-5	1.9%	0.67%	1 micron	11.8	5.8/12.0/108	683	8.2	83
5-6	1.9%	0.67%	1 micron	5.6	7.4/10.9/108	478	6.7	71
5-7	2.1%	0.74%	0.05micron	5.4	6.6/11.6/117	496	6.7	74
5-8	2.1%	0.74%	0.05 micron	5.9	5.4/12.8/100	431	6.2	69

[1]Tenacity (gpd), Elongation (%), Modulus (gpd), measured using ASTM test method D-3822.

[2]Cut Protection Performance, measured using the Ashland CPP test.

[3]Ounces per Square Yard.

We claim:

1. A cut-resistant fiber comprising a fiber-forming polymer and a hard filler distributed uniformly in said fiber, said filler having a Mohs Hardness value greater than about 3, said filler being present in an amount of about 0.05% to about 20% by weight; said fiber having improved cut resistance compared with a fiber comprising said polymer without said filler.

2. A cut-resistant fiber as recited in Claim 1, wherein the cut resistance of said fiber is improved by at least about 10% compared with a fiber comprising said polymer without said filler.

3. A cut-resistant fiber as recited in Claim 1, wherein said hard filler has a Mohs Hardness value greater than about 5.

4. A cut-resistant fiber as recited in Claim 1, wherein said hard filler is present in an amount of about 0.01% to about 3% by volume.

5. A cut-resistant fiber as recited in Claim 2, wherein said hard filler is present in an amount of about 0.03% to about 1.5% by volume.

6. A cut-resistant fiber as recited in Claim 2, wherein said hard filler is present in an amount of about 0.05% to about 1% by volume.

7. A cut-resistant fiber as recited in Claim 1, wherein said hard filler is selected from the group consisting of a powder having an average diameter up to about 20 microns, an elongated particle having an average length up to about 20 microns, and mixtures thereof.

8. A cut-resistant fiber as recited in Claim 2, wherein said hard filler is selected from the group consisting of a powder having an average diameter in the range of about 0.05 to about 5 microns, an elongated particle having an average length in the range of about 0.05 to about 5 microns, and mixtures thereof.

9. A cut-resistant fiber as recited in Claim 2, wherein said hard filler is selected from the group consisting of a powder having an average diameter in the range of about 0.2 to about 2 microns, an elongated particle having an average length in the range of about 0.2 to about 2 microns, and mixtures thereof.

10. A cut-resistant fiber as recited in Claim 1, wherein said hard filler is present in an amount of about 0.01% to about 3% by volume; wherein said hard filler is selected from the group consisting of a powder having an average diameter up to about 20 microns, an elongated particle having an average length up to about 20 microns, and mixtures thereof.

11. A cut-resistant fiber as recited in Claim 2, wherein said hard filler is present in an amount of about 0.03% to about 1.5% by volume; wherein said hard filler is selected from the group consisting of a powder having an average diameter in the range of about 0.05 to about 5 microns, an elongated particle having an average length of about 0.05 to about 5 microns, and mixtures thereof.

12. A cut-resistant fiber as recited in Claim 2, wherein said hard filler is present in an amount of about 0.05% to about 1% by volume; wherein said hard filler is selected from the group consisting of a

powder having an average diameter in the range of about 0.2 to about 2 microns, an elongated particle having an average length of about 0.2 to about 2 microns, and mixtures thereof.

13. A cut-resistant fiber as recited in Claim 2, wherein said hard filler is a metal or metal alloy.

14. A cut-resistant fiber as recited in Claim 13, wherein said hard filler is a metal or metal alloy selected from the group consisting of iron, nickel, stainless steel, tungsten, and mixtures thereof.

15. A cut-resistant fiber as recited in Claim 2, wherein said hard filler is a non-metal selected from the group consisting of metal oxides, metal carbides, metal nitrides, metal sulfides, metal silicates, metal silicides, metal sulfates, metal phosphates, metal borides, and mixtures thereof, except that said hard filler is not titanium dioxide or silicon dioxide.

16. A cut-resistant fiber as recited in Claim 1, wherein said fiber-forming polymer is a liquid crystalline polymer.

17. A cut-resistant fiber as recited in Claim 2, wherein said fiber-forming polymer is a lyotropic liquid crystalline polyamide comprising monomer units derived from terephthalic acid and 1,4-phenylene-diamine.

18. A cut-resistant fiber as recited in Claim 1, wherein said fiber-forming polymer is a thermotropic liquid crystalline polymer.

19. A cut-resistant fiber as recited in Claim 18, wherein said thermotropic liquid crystalline polymer comprises one or more monomer units derived from monomers selected from the group consisting of terephthalic acid, isophthalic acid, 1,4-hydroquinone, resorcinol, 4,4'-dihydroxybiphenyl, 4,4'-biphenyldicarboxylic acid, 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 2,6-naphthalenedicarboxylic acid, 2,6-dihydroxynaphthalene, 4-aminophenol, and 4-aminobenzoic acid.

20. A cut-resistant fiber as recited in Claim 19, wherein said hard filler is a metal or metal alloy.

21. A cut-resistant fiber as recited in Claim 19, wherein said hard filler is a non-metal selected from the group consisting of metal oxides, metal carbides, metal nitrides, metal sulfides, metal silicates, metal silicides, metal sulfates, metal phosphates, metal borides, and mixtures thereof.

22. A cut-resistant fiber as recited in Claim 12, wherein said fiber-forming polymer is a thermotropic liquid crystalline polymer.

23. A cut-resistant fiber as recited in Claim 22, wherein said thermotropic liquid crystalline polymer comprises monomer units derived from 6-hydroxy-2-naphthoic acid and 4-hydroxybenzoic acid.

24. A cut-resistant fiber as recited in Claim 23, wherein said hard filler is a metal or metal alloy selected from the group consisting of iron, steel, nickel, tungsten, and mixtures thereof.

25. A cut-resistant fiber as recited in Claim 24, wherein said hard filler is tungsten in an amount of about 1% to about 2% by weight.

26. A cut-resistant fiber as recited in Claim 23, wherein said hard filler is a non-metal selected from the group consisting of metal oxides, metal carbides, metal nitrides, metal sulfides, metal silicates, metal silicides, metal sulfates, metal phosphates, metal borides, and mixtures thereof.

27. A cut-resistant fiber as recited in Claim 26, wherein said hard filler is alumina.

28. A cut-resistant fiber as recited in Claim 1, wherein said fiber-forming polymer is a melt-processable isotropic semicrystalline polymer.

29. A cut-resistant fiber as recited in Claim 2, wherein said fiber-forming polymer is a melt-processable isotropic semicrystalline polymer selected from the group consisting of poly(alkylene terephthalates), poly(alkylene naphthalates), poly(arylene sulfides), aliphatic polyamides, aliphatic-aromatic polyamides, and polyesters of cyclohexanedimethanol and terephthalic acid.

30. A cut-resistant fiber as recited in Claim 12, wherein said fiber-forming polymer is a semicrystalline polymer selected from the group consisting of poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate), poly(phenylene sulfide), poly(1,4-cyclohexanedimethanol terephthalate), nylon-6, and nylon-66.

31. A cut-resistant fiber as recited in Claim 30, wherein said hard filler is a metal or metal alloy.

32. A cut-resistant fiber as recited in Claim 30, wherein said hard filler is a non-metal selected from the group consisting of metal oxides metal

carbides, metal nitrides, metal sulfides, metal silicates, metal silicides, metal sulfates, metal phosphates, metal borides, and mixtures thereof, except that said hard filler is not titanium dioxide or silicon dioxide.

33. A cut-resistant fiber as recited in Claim 30, wherein said fiber-forming polymer is poly(ethylene terephthalate).

34. A cut-resistant fiber as recited in Claim 33, wherein said hard filler is a metal or metal alloy selected from the group consisting of iron, steel, nickel, tungsten, and mixtures thereof.

35. A cut-resistant fiber as recited in Claim 34, wherein said hard filler is tungsten in an amount of about 10% by weight.

36. A cut-resistant fiber as recited in Claim 33, wherein said hard filler is a non-metal selected from the group consisting of metal oxides metal carbides, metal nitrides, metal sulfides, metal silicates, metal silicides, metal sulfates, metal phosphates, metal borides, and mixtures thereof, except that said hard filler is not titanium dioxide or silicon dioxide.

37. A cut-resistant fiber as recited in Claim 33, wherein said hard filler is alumina.

38. A cut-resistant fiber as recited in Claim 2, wherein said fiber has a denier in the range of about 1 to about 50 dpf.

39. A cut-resistant fiber as recited in Claim 2, wherein said fiber is a monofilament.

40. A composite yarn having improved cut resistance comprising the cut-resistant fiber of Claim 1 and a reinforcing inorganic fiber.

41. The composite yarn recited in Claim 40, wherein said reinforcing inorganic fiber is selected from the group consisting of metal fiber, ceramic fiber and glass fiber.

42. A composite yarn having improved cut resistance comprising the cut-resistant fiber of Claim 11 and a reinforcing inorganic fiber selected from the group consisting of metal fiber, ceramic fiber and glass fiber.

43. A method of making cut-resistant fabric comprising the steps of:

(a) making a uniform blend of a fiber-forming polymer and about 0.05% to about 20% by weight of a hard filler having a Mohs Hardness value greater than about 3;
(b) spinning said uniform blend into a fiber or yarn; and
(c) fabricating said fiber or yarn into fabric having improved cut resistance in comparison with the same fabric made from said fiber-forming polymer without said hard filler, said fabric optionally comprising other thermoplastic fibers or reinforcing inorganic fibers selected from the group consisting of ceramic, metal and glass fibers.

44. The method as recited in Claim 43, wherein said uniform blend comprises about 0.03% to about 1.5% by volume of a hard filler selected from the group consisting of a powder having an average diameter in the range of about 0.05 microns to about 5 microns, an elongated particle having an average length in the range of about 0.05 microns to about 5 microns, and mixtures thereof.

45. The method as recited in Claim 43, wherein said uniform blend comprises about 0.05% to about 1% by volume of a hard filler selected from the group consisting of a powder having an average diameter in the range of about 0.2 microns to about 2 microns, an elongated particle having an average length in the range of about 0.2 microns to about 2 microns, and mixtures thereof, wherein the cut resistance of said fabric is improved by at least about 10% compared with the cut resistance of the same fabric made without said hard filler.

46. The method as recited in Claim 44, wherein said fiber-forming polymer is a liquid crystalline polymer.

47. The method as recited in Claim 44, wherein said fiber-forming polymer is a lyotropic liquid crystalline polyamide comprising monomer units derived from terephthalic acid and 1,4-phenylenediamine.

48. The method as recited in Claim 44, wherein said fiber-forming polymer is a thermotropic liquid crystalline polymer.

49. The method as recited in Claim 45, wherein said fiber-forming polymer is a thermotropic liquid crystalline polymer comprising monomer units derived from 6-hydroxy-2-naphthoic acid and 4-hydroxybenzoic acid.

50. The method as recited in Claim 49, wherein said hard filler is a metal or metal alloy.

51. The method as recited in Claim 50 wherein said hard filler is selected from the group consisting of iron, steel, tungsten and nickel.

52. The method as recited in claim 51, wherein said hard filler is tungsten in an amount of about 1% to about 2% by weight.

53. The method as recited in Claim 49, wherein said hard filler is a non-metal selected from the group consisting of metal oxides, metal carbides, metal nitrides, metal sulfides, metal silicates, metal silicides, metal sulfates, metal phosphates, metal borides, and mixtures thereof.

54. The method as recited in Claim 44, wherein said fiber-forming polymer is a melt-processable isotropic semi-crystalline polymer selected from the group consisting of poly(alkylene terephthalates), poly(alkylene naphthalates), poly(arylene sulfides), aliphatic polyamides, aliphatic-aromatic polyamides, and polyesters of cyclohexanedimethanol and terephthalic acid.

55. The method as recited in Claim 45, wherein said fiber-forming polymer is a melt-processable semicrystalline polymer selected from the group consisting of poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene naphthalate), poly(phenylene sulfide), poly(1,4-cyclohexanedimethanol terephthalate), nylon-6, and nylon-66.

56. The method as recited in Claim 55, wherein said fiber-forming polymer is poly(ethylene terephthalate).

57. The method as recited in Claim 56, wherein said hard filler is a metal or metal alloy.

58. The method as recited in Claim 57, wherein said hard filler is tungsten in an amount of about 10% by weight.

59. The method as recited in Claim 56, wherein said hard filler is a non-metal selected from the group consisting of metal oxides, metal carbides, metal nitrides, metal sulfides, metal silicates, metal silicides, metal sulfates, metal phosphates, metal borides, and mixtures thereof.

60. The method as recited in Claim 59, wherein said hard filler is alumina.

61. Cut-resistant fabric made by the method of Claim 43.

62. Cut-resistant fabric made by the method of Claim 52.

63. Cut-resistant fabric made by the method of Claim 58.

INTERNATIONAL SEARCH REPORT

Intern. ...al Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D01F1/10 D01F6/84 D01F6/62 D01F6/60 C08K3/08
C08K3/22 A41D13/10 A41D31/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D01F C08K A41D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 599 231 (HOECHST CELANESE CORP) 1 June 1994 see the whole document ---	1-14, 18-20, 22-25, 38-45, 48-52, 61,62
X	EP,A,0 376 323 (KAWASAKI STEEL CO) 4 July 1990 see the whole document ---	1-15, 18-22, 24,26, 27, 43-45, 48,50, 51,53, 61,62
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Tarrida Torrell, J

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INTERNATIONAL SEARCH REPORT

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